CRYSTAL NUCLEATION IN LITHIUM BORATE GLASS

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ABSTRACT

Crystal nucleation measurements were made on three lithium borate compositions in the vicinity of $Li_2O \cdot 2B_2O_3$. All nucleation measurements were performed at 500°C. Certain aspects of the nucleation behavior indicated (tentatively) that it proceeded by a homogeneous mechanism. The steady state nucleation rate was observed to have the largest value when the Li_2O concentration was slightly in excess of the diborate composition. The change in nucleation rate with composition is controlled by the variation of viscosity as well as the change in free energy with composition. The variation of nucleation rate is explained qualitatively in these terms.

INTRODUCTION

Homogeneous crystal nucleation is a process of extreme scientific interest and technological importance to the field of glass science. It is fundamental to the description of glass forming (1). However, gaps exist in the basic understanding of nucleation phenomena in glasses (2,3). The technological significance of bulk crystal nucleation stems from the central role it plays in glass ceramic formation (4).

Previous studies of homogeneous crystal nucleation in simple glass have involved silicate compositions (5-10). Also, in all cases where quantitative comparisons were made between theory and experiment (7-10), the theoretically predicted rates were many orders of magnitude too small.

Herein, we present our findings on the volume crystal nucleation in a simple binary borate glass system. To our knowledge, it is the first such study performed and reported in the literature.

Borate glasses, in general, do not have the technological importance of silicate glasses, but they are of great interest scientifically. This interest stems in large part from the structural complexity of borate glasses. Although there is not complete agreement concerning the structure of silica (and silicate glasses), the random network theory proposed and substantiated by Zachariasen (11), and Warren (12,13) is widely accepted. The SiO_4 tetrahedron is the basic building block of silica

and silicate glasses in the theory. On the other hand, boron may assume 3 or 4 fold coordination in borate glasses. Also, it is believed that borate glasses are constructed with the aid of several basic structural units (14). The number and ratio of structural units present in a given borate is a function of glass composition. Thus, borate glasses exhibit a much richer array of structural configurations than silicates.

It might be expected that these structural differences could produce contrasting crystal nucleation behavior in borate and silicate glasses. For example, the tendency to form short-lived metastable crystalline structures may be quite sensitive to the details of glass structure. Such anticipated possible features stimlated the present study.

EXPERIMENTAL AND AUXILLIARY MEASUREMENTS

Three lithium borate glasses were prepared by standard glassmaking methods. The glasses were chemically analyzed (for Li) with the aid of atomic absorption and refractive index measurements. The composition of the glasses, in mole % Li_2O, were determined as 33.8 (designated as glass Q), 36.8 (glass G), and 38.2 (glass H).

The hydroxyl ion concentration for each glass was measured using IR spectroscopy. It was found that the OH content of the glasses were comparable, and present in low concentration ($\sim$ .05 mol %).

X-ray diffraction measurements were made of the

nucleated glasses as well as of the fully crystallized glasses. In all cases, where crystallization could be detected by X-ray analysis, the crystalline species was identified as $Li_2O \cdot 2B_2O_3$.

Differential Scanning Calorimetry (DSC) measurements were made of each composition in the heat-up mode from room temperature to 600°C in an air atmosphere. A portion of a typical DSC scan is shown in Fig. (1), where a heating rate of 5 deg.C/min. was used. A single exotherm, corresponding to crystallization, occurs at approximately 525°C. Also, one notes that the glass transition temperature appears to be located in the vicinity of 469°C.

In view of the above findings a nucleation temperature of 500°C was chosen. Glass samples, free from crystallites as determined via examination with a polarizing microscope, were heated in platinum boats using a tube furnace. The furnace employed has an isothermal zone constant to ± 1°C. The samples were ground and polished after receiving appropriate heat treatment. They were polished to a thickness of 122-290 μm, which was appropriate for the maximum crystallite concentration observed. Diamond stop carriers were used to insure that the faces were parallel and flat. Then, the samples were examined with the aid of an Olympus polarizing microscope, and at least 10 optical micrographs were obtained for each sample. The particle number was determined directly by counting the crystals in from 6 to 10 of the frames from each glass. Knowledge of

the magnification and thickness of the glass allowed the determination of the crystallite number density present within it.

NUCLEATION MEASUREMENTS AND RESULTS

Nucleation measurements are usually performed via two stage heat treatments (7). This method consists of a low temperature heating of the glass to produce the nuclei, followed by a high temperature heating to grow the nuclei to an observable size. This procedure is required when the nucleation curve (I(T) vs. T; where T is temperature, and I the nucleation rate) has little overlap with the growth curve. A potential disadvantage of this method is that some of the nuclei may disappear when heated at the growth temperature. This results from the fact that the critical radius is inversely proportional to the bulk free energy difference between crystal and liquid. The magnitude of the latter is smaller at the growth temperature, and thus the critical radius is larger at the growth temperature than at the nucleation temperature. Thus, those particles whose radii fall between these two limits will dissolve. Hence, using a two stage heat treatment tends to underestimate the nucleation rate. James (7), however, has observed that this is not a very serious problem, at least in the case of $Li_2O \cdot 2SiO_2$ crystal nucleation.

In the present situation the particles were observed to grow sufficiently rapidly at the nucleation temperature

to grow sufficiently rapidly at the nucleation temperature so that a single stage heating sufficed to determine the particle density (and nucleation rate). This procedure does not suffer from the difficulty described above. However, the single stage heat treatment could potentially lead to underestimation of the particle number, too, since a certain fraction of the nuclei which form will be too small to observe. For the present measurements, it will be demonstrated that this problem will introduce a negligible error in the steady state number density and no error in the measured steady state nucleation rate. Let us assume that particles with radii r less than r_o cannot be observed. Also, one may divide the actual number density of particles present, N_{true}, into two parts; N_{exp} , the number density measured, and N_x the correction term due to unobservable particles. Thus,

$$N_{true} = N_x + N_{exp} \tag{1}$$

It is clear that at any time, t

$$N_x = \int_{t^*}^{t} I(t')dt' \tag{2a}$$

with t^* defined by

$$g(t-t^*) = r_o \tag{2b}$$

where g is the crystal growth rate. Since I = dN/dt,

$$I_{true} = I_{exp} + I(t) - I\,(t'-r_o/g) \qquad (3a)$$

Also, since $I(t) = I_{true}$,

$$I_{exp} = I(t-r_o/g) \qquad (3b)$$

If there are not transient effects at the temperature of measurement, then $I(t-r_o/g)$ is independent of time and is the true nucleation rate. If transient effects are present, but one only considers those experimental points corresponding to steady state nucleation, then I_{exp} is time independent, and clearly equal to the true steady state nucleation rate. Thus, unobserved particles do not contribute to the nucleation rate.

Now the correction to the particle density is considered. Using eqs (1) and (2a),

$$N_{true} = \int_{t^*}^{t} I(t')dt' + N_{exp} \qquad (4)$$

However, since it has been shown that $I(t) = I^o$(steady state rate) for $t \geq t^*$, eq (4) reduces to

$$N_{true} = (t-t^*)I^o + N_{exp} = (r_o/g)I^o + (t-t_c^e)I^o \qquad (4')$$

where eq (2b) has been used and t_c^e is the experimental value of the intercept on the time axis. In the steady state region $N_{true} = I^o(t-t_c^a)$, where t_c is the true time axis intercept of the steady state line. Hence,

$$t_c^a = t_c^e - r_o/g \qquad (5)$$

It will be shown subsequently that $t_c^e >> r_o/g$, and thus there are negligible corrections to the time axis intercepts and number densities associated with the experimental plots.

The experimentally determined number densities as a function of heating time are shown as the points in figs (2)-(4). The straight lines represent the least squares fit to these data. For glasses H and Q the points for the longest times, 75 and 240 minutes, respectively, were excluded in the calculations of the least-squares lines. This was justified by the significantly higher correlation coefficient values thus obtained. Physically, this may indicate that at the longest times sufficiently rapid and extensive crystallization occurred to raise the sample temperature above the ambient furnace temperature. The equations of these calculated lines and correlation coefficients are shown in Table 1. It is clear that the measurements correspond to the steady state regions. The bars on the points correspond to the root-mean-square errors (standard deviations) of the individual measurements. These were obtained for each point by taking into account the multiple measurements made for N_v at each time corresponding to different optical micrographs of the sample section.

The slopes of the curves are the steady state

nucleation rates. They are reported in Table 2, along with the experimentally determined values of t_c^e, the time axis intercepts of the number density vs. time plots. Also, the calculated errors for the latter quantities are indicated. The error analysis was performed by usual statistacal methods, and utilized the calculated standard deviations associated with each number density.

DISCUSSION

It is tempting to proclaim that the bulk nucleation observed in these lithium borate glasses is homogeneous in nature. More nucleation data is required, however, to bolster such a claim. Nevertheless, there does exist one strong indication that the crystal nucleation occurred homogeneously; namely the magnitude of the nucleation rate. For comparative purposes we rely upon the findings of James (2). He noted that for the few silicate glasses which are believed to nucleate homogeneously the ratio of T_d, the temperature at which the nucleation rate is 1 $cm^{-3}sec^{-1}$ (barely detectable) to Tm (the melting temperature) ranges from .62 to .66. For glass Q, T_d/Tm =.64, and the measured nucleation rate is ≈ 165 $cm^{-3}sec^{-1}$. Hence, the nucleation rate in this glass is comparatively large, which is a leading indication of homogeneous nucleation.

From an inspection of figs (2)-(4), it is noted that the N(t) plots do not intersect the origin, but that they

cut the time axis at positive times (see also column 3 of Table 2). This implies the existence of transient nucleation effects. However, eq (5) shows that the actual values of the time axis intercepts are smaller than the observed ones. Thus, in order to demonstrate the existence of transient effects at this temperature, estimates must be made of r_o/g. It may be recalled that r_o is the smallest visible crystallite. It is estimated that $r_o \approx 2\ \mu m$. The crystal growth rates, g, have not been measured, but it is possible to obtain lower bounds on the growth rates which will place upper bounds on the magnitude of r_o/g. If one measures the size of the largest crystallite in the sample and assumes that its growth started at t=0, this will yield a lower bound on g. Lower limits to the growth rates determined in this manner are shown in column 4 of Table 2. Then simple calculations show that r_o/g is even smaller than the uncertainty in t_c^e for each glass. This establishes the presence of transient effects.

Finally, the change in nucleation rate with composition is considered. James (15) has discussed the anticipated effects of composition variations upon the nucleation rate based upon the classical nucleation expression

$$I = A/\eta \exp\ (-\ b\sigma^3/(\Delta G_v)^2 kT) \qquad (6)$$

In eq. (6), η is the viscosity, σ is the crystal-glass surface tension, T is the temperature, ΔG_v is the bulk free

energy difference between crystal and glass per unit volume, k is the Boltzmann constant, and A and b are constants. Although eq (6) was derived for a one component (or pseudo one component) system and its use is strictly not correct for "off-composition" nucleation, it should be capable of predicting qualitative trends (especially if the composition shift is small). The change in the nucleation rate with composition can be considered by inspecting the anticipated changes in η , ΔG_V, and σ with composition. If one considers a small composition shift away from a compound in a binary system, then by standard thermodynamic arguments (16) it can be shown that the magnitude of ΔG (bulk free energy difference between crystal and liquid) will decrease. In other words, the largest thermodynamic driving force for nucleation will occur at the composition of the compound, and compositional shifts in either direction will tend to make ΔG_V (and thus I) smaller. On the other hand, the nucleation rate is a monotonically decreasing function of viscosity, if all other parameters are held fixed. Therefore, compositonal shifts which decrease (increase) η will increase (decrease) I. For binary alkali silicate systems this implies that a positive compositional shift (adding more R_2O) will tend to increase the nucleation rate while a negative shift will have the opposite effect. Unfortunately, not much is known about the composition dependence of σ , although James speculates that it will be smaller if there is no

compositional shift. If this is correct, then this would tend to enhance the nucleation rate of the compound composition in comparison to the rates of compositions with either positive or negative compositional shifts.

There have been several experimental studies on the effects of compositional variations on the nucleation rate in silicate glasses (5,8,9). Gonzalez-Oliver (8) considered the influence on the nucleation rate of small compositional shifts from $Na_2O \cdot 2C_aO \cdot 3SiO_2$ (NC_2S_3) glass. He investigated six glasses, each containing a ±1 mole% variation of one of the major constituents. The largest effect upon the nucleation rate was caused by the Na_2O variation, with an increase in the nucleation rate for the glass with the 1% extra Na_2O and a decrease in I for the -1% Na_2O containing glass. Also, it was observed that these glasses exhibited the smallest and largest viscosities, respectively, too. Thus, for small composition changes from NC_2S_3 the variation in the nucleation rate is primarily controlled by the viscosity change.

Burnett and Douglas (5) investigated the nucleation and crystallization behavior of glass in the Na_2O-BaO-SiO_2 system. They ascertained that nucleation diminished as one moved from the stoichiometric barium disilicate composition. This implies that either a decrease in ΔG_V or an increase in σ is the controlling factor in this system rather than the viscosity.

James (15) has concluded that for the interpretation

of the change in nucleation kinetics with composition, one probably must take into account all three factors simultaneously since variations in the nucleation rate are unlikely to be a function of solely one of the variables.

The change in nucleation rate with composition near the $Li_2O \cdot 2B_2O_3$ composition is shown in Table 2. One observes that as the Li_2O content increases the nucleation rate first increases and then decreases. The interpretation of these results is subject to even more uncertainty than in the previous cases because of two additional unknowns. First, viscosity data are not available in the high Li_2O composition glasses due to their rapid crytallization rates. Next, unlike the alkali silicate glasses whose viscosities decrease with increasing alkali concentration, the composition dependence of the viscosities of the alkali borate glasses exhibit minima and maxima (17). Despite these additional uncertainties one may postulate an explanation, albeit speculative, of the present results. Although the behavior of the viscosity as a function of composition of the glasses considered herein is uncertain, it is quite reasonable to assume that it is decreasing with increasing Li_2O content. This assumption results from an inspection of fig (2) of ref (17) which shows that the local maximum in viscosity as a function of R_2O at temperatures of 600, 700, 800, and 900°C all occur in the region of 20 mole%. Therefore, a reasonable explanation of the data is as

follows. The change in viscosity with composition is probably greater than the variations in ΔG_v or σ. However, from an inspection of eq. (6) one notes that I is a much more sensitive function of ΔG or σ than of η. Therefore, although the change in η is probably dominant over the entire composition region, the strong dependence of I on ΔG and σ is dominant for larger composition variations causing an eventual decline in nucleation rate. This argument can be given further credence by an inspection of the behavior of the transient time, τ (18). It is easy to demonstrat that τ follows the behavior of t_c (i.e. τ decreases when t_c decreases). Therefore, from column 3 of Table 2, one concludes that τ decreases as the Li_2O concentration increases. However, τ has the following dependence upon the crucial parameters η, ΔG_v, and σ (15),

$$\tau \sim \eta\left(\frac{\sigma}{(\Delta G_v)^2}\right) \qquad (7)$$

Since τ decreases with increasing composition, the viscosity change must predominate since ΔG decreases and σ is believed to increase. Thus, the behavior of the transient time with composition is consistent with our interpretation of the variation of the nucleation rate with increasing Li_2O content.

SUMMARY

The bulk nucleation of three glass compositions in the vicinity of $Li_2O \cdot 2B_2O_3$ was examined. Steady state nucleation rates were determined as a function of composition, and it was observed that at + 3% composition variations in Li_2O caused an increase in rate but a +4.2% increase in Li_2O evoked a decline in nucleation rate. This behavior could be plausibly explained in terms of the combined effects of viscosity, free energy, and surface tension changes. It was observed that the nucleation exhibited transient behavior for all compositions. Finally, evidence was provided which led one to suspect that the nucleation occurred homogeneously. However, additional studies are required to confirm this conjecture.

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TABLE 1

FIT OF EXPERIMENTAL NUMBER DENSITY DATA

Glass	Mole% Li_2O	Equation of line (Figs (2)-(4)) 10^{-4}	Correlation Coefficient
Q	33.8	$N_v = .86t - 72.34$	.943
G	36.8	$N_v = 1.692t - 31.73$	.979
H	38.2	$N_v = .25t - 1.37$	.995

TABLE 2

SUMMARY OF EXPERIMENTAL RESULTS

Glass (Mole% Li_2O)	Nucleation Rate $(cm^3\text{-}min)^{-1}$	t_c^e(min)	Lower Limit to Growth Rate (μm/min)
O (33.8)	(.86 ± .14) X 10^4	84 ± 4.4	.73
G (36.8)	(1.69 ± .26) X 10^4	19 ● 2	3.5
H (38.2)	(.25 ± .03) X 10^4	5.6 ± 1.9	4.2

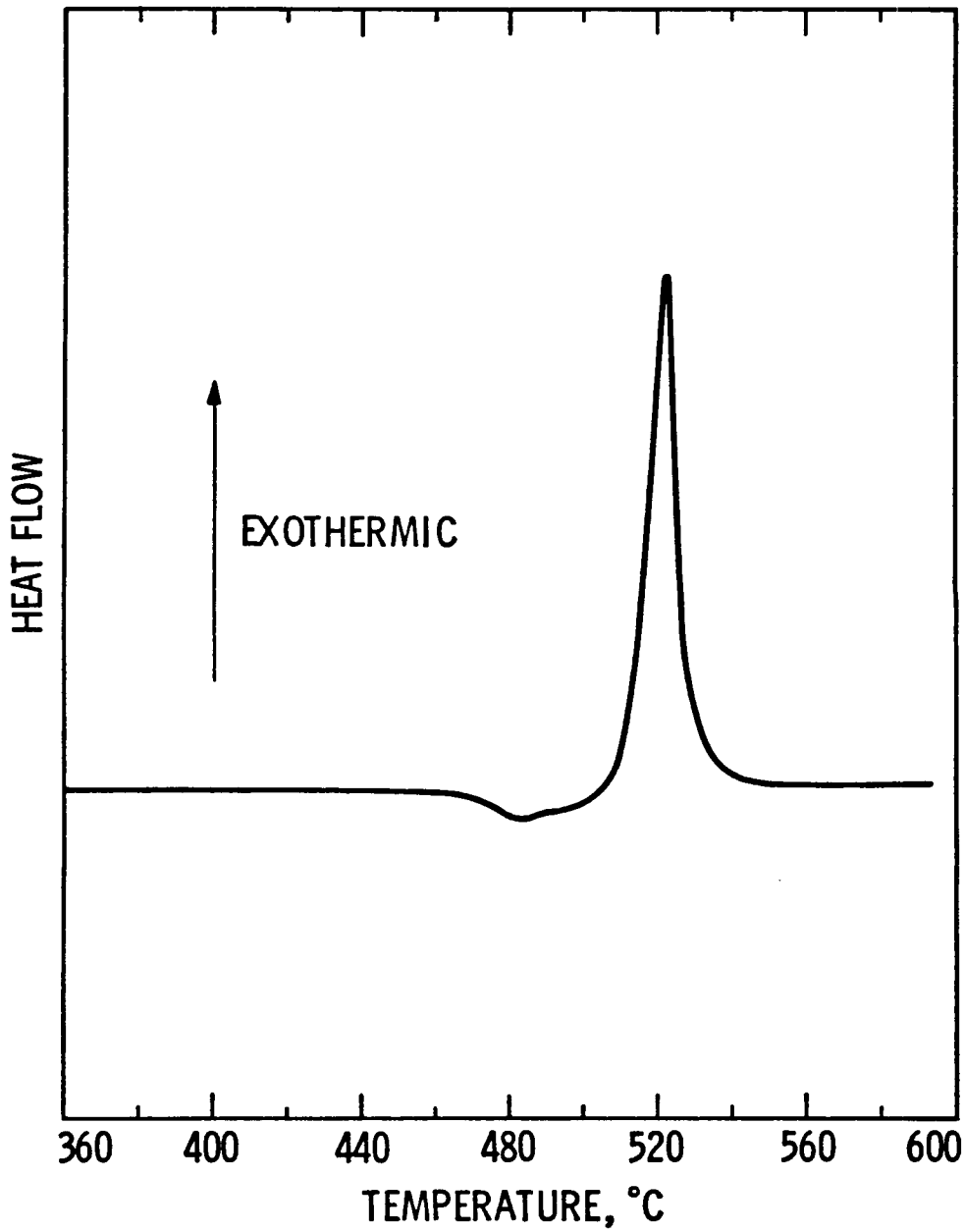

Figure 1 Differential Scanning Calorimetry scan of glass H, heated in air at a rate of 5°C/min.

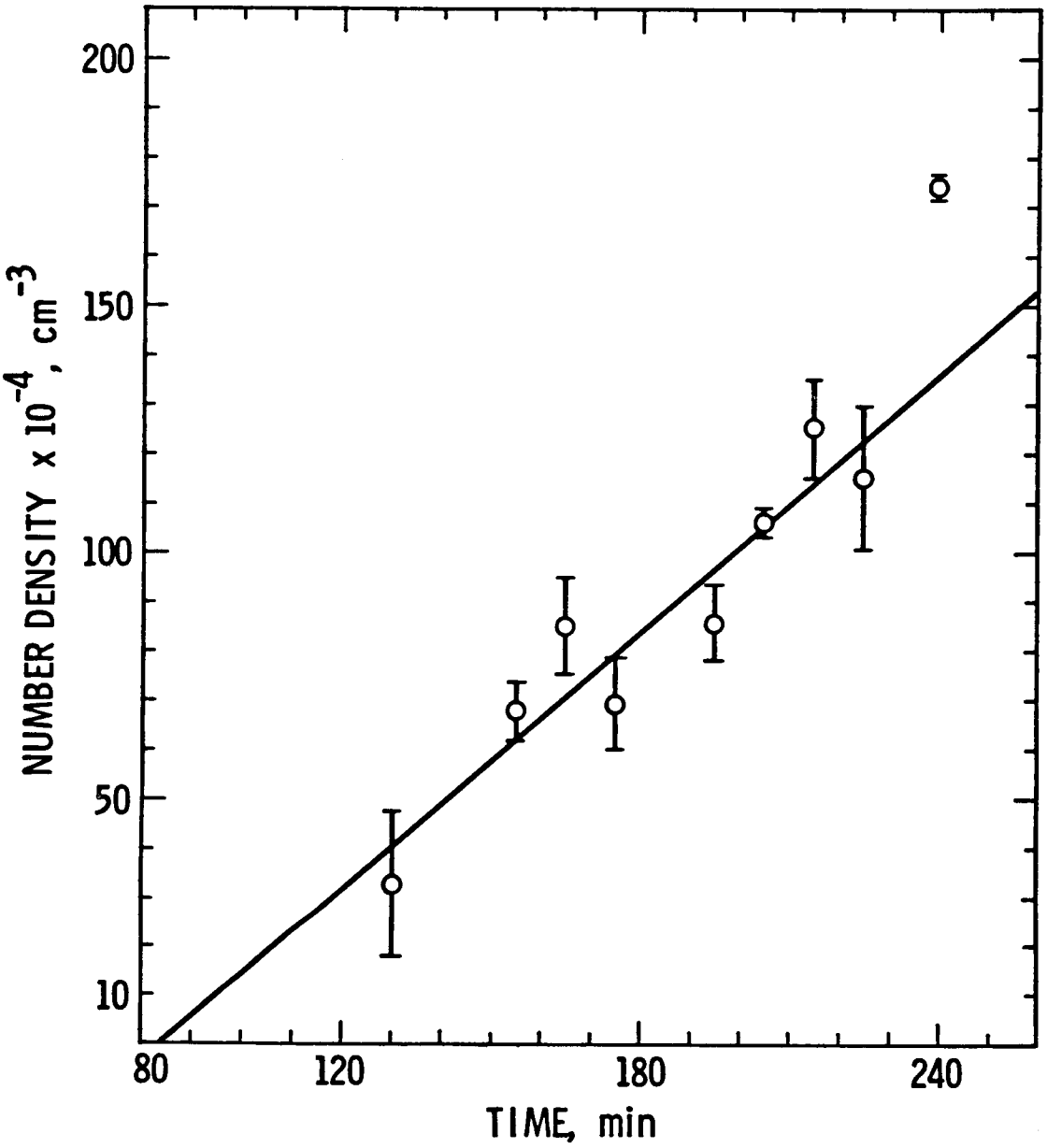

Figure 2 Crystal number density as a function of time for glass Q (33.8 mole% Li_2O). Glass was heated at 500°C.

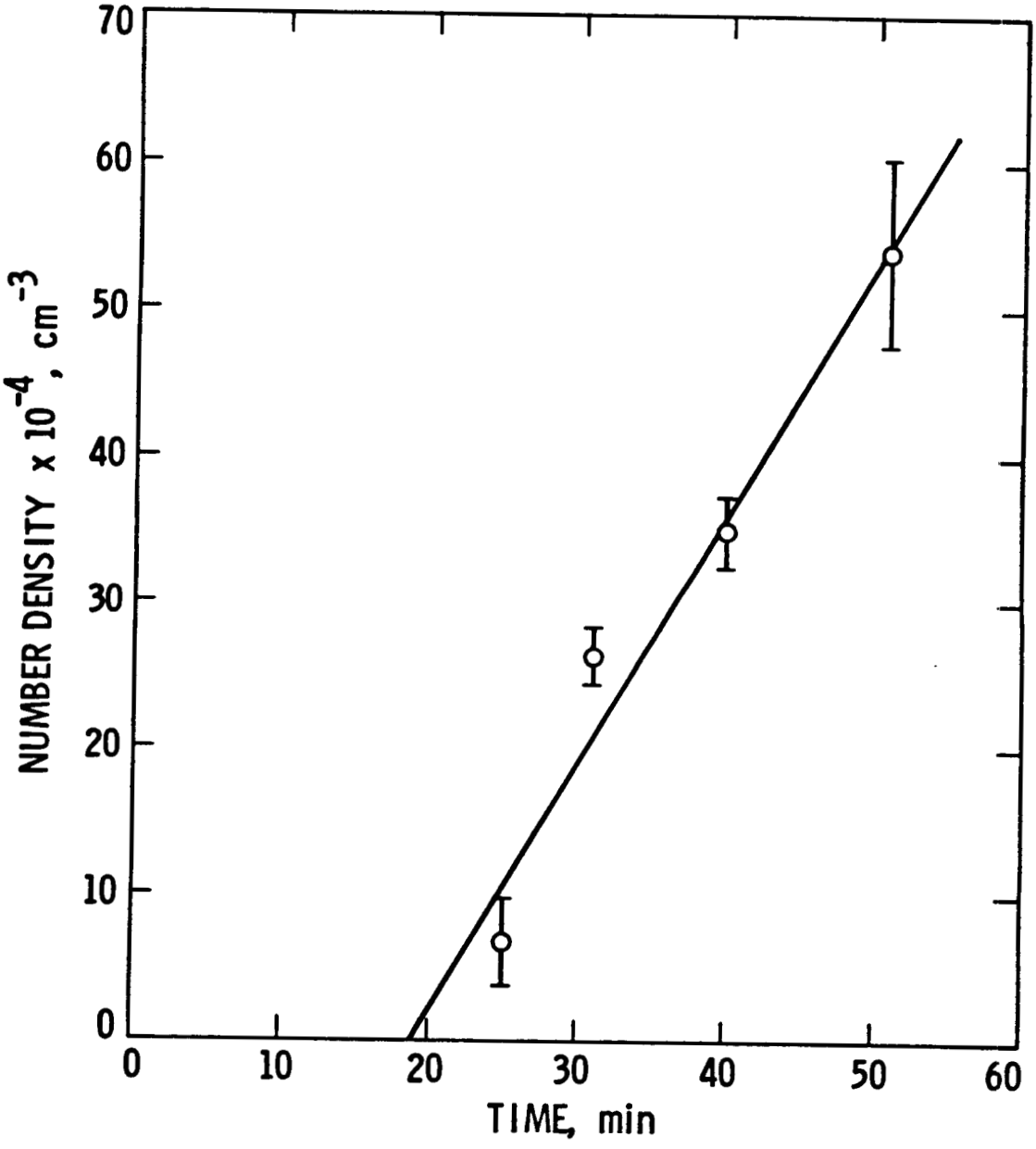

Figure 3 Crystal number density as a function of time for glass G (36.8 mole% Li_2O). Glass was heated at 500°C.

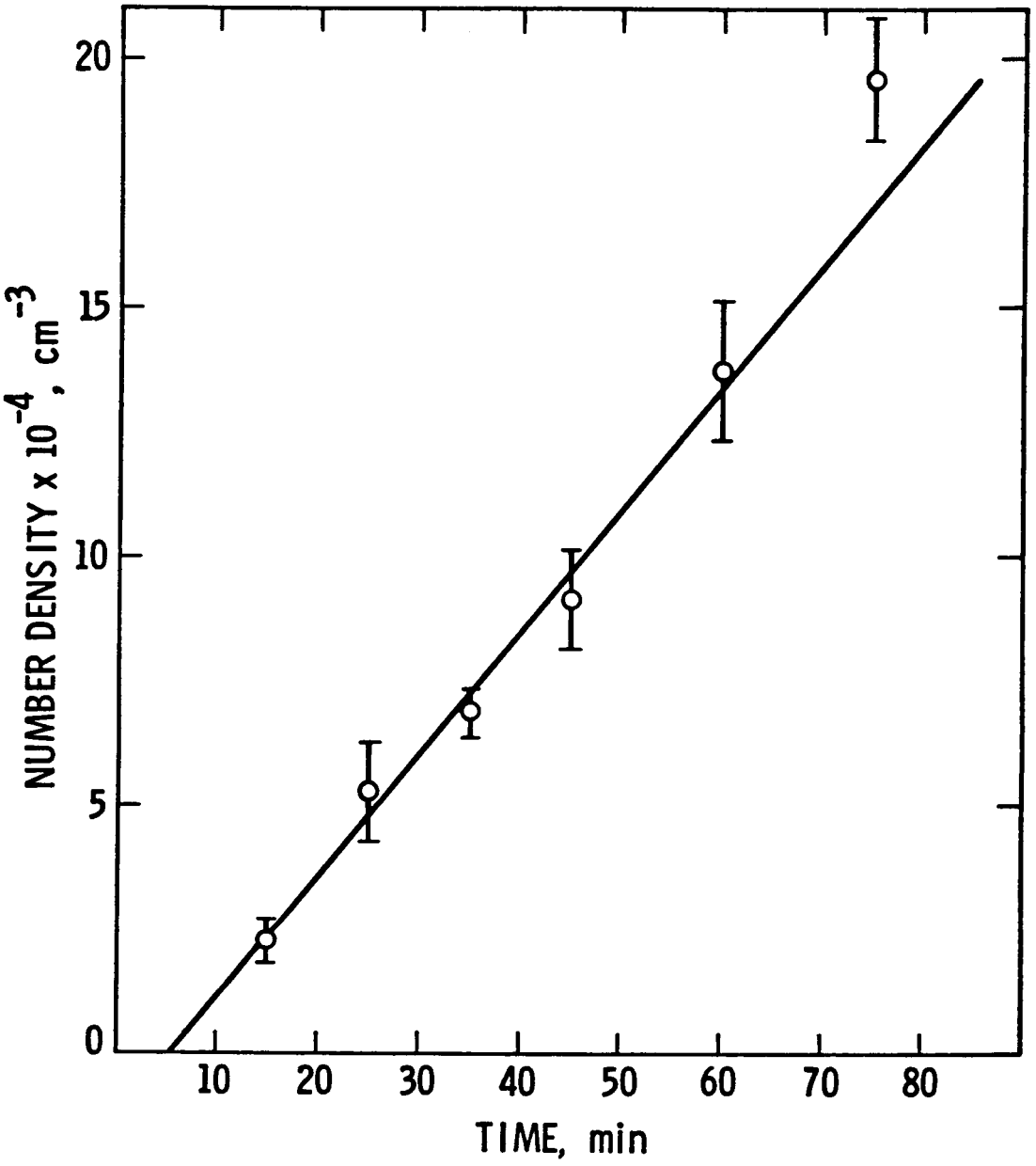

Figure 4 Crystal number density as a function of time for glass H (38.2 mole% Li_2O). Glass was heated at 500°C.